Scale-up and Testing of Advanced Materials from the BATT Program

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ES029)

Overview

Timeline

- Start: 10/2009
- End: 9/2013
- Percent complete: 87.5

Budget

- Total project funding:

  $760 k

  (DOE Share: 100 %)
- Funding received in FY12:

  $ 190 k
- Funding for FY13:

  $190 k

Barriers

- Barriers / Targets addressed
  - Cost - System = 100 $/kWh
  - Performance - Power:Energy = 2:1
  - Life - Deep discharge cycles = 750

Partners

- NEI
- Daikin
- Umicore
- Conoco Phillips
- Timcal
- Celgard
- ANL
- SNL
- CWRU
- U. Texas

Relevance / Objectives

- Objective for 2012-2013:
  - Using high-quality coin cells, evaluate materials as they are developed in the BATT program and compare to an industry standard.
  - Evaluate materials for a baseline $LiNi_{1/2}Mn_{3/2}O_4$ system for ABR and BATT.

- Relevance to Vehicle Technology Program:
  - This provides a mechanism for measuring progress within the Program.
  - Both the more applied and more fundamental Programs are interested in high-voltage cathodes to find a path to high energy.

- Impact on barriers:
  - Allows DOE to track progress toward energy density and cycle life goals.

Milestones

- **Test a number of BATT materials and present at the DOE AMR.**
- **Test a number of materials for the high-voltage cathode system for ABR and BATT and report at DOE AMR.**

Approach/Strategy

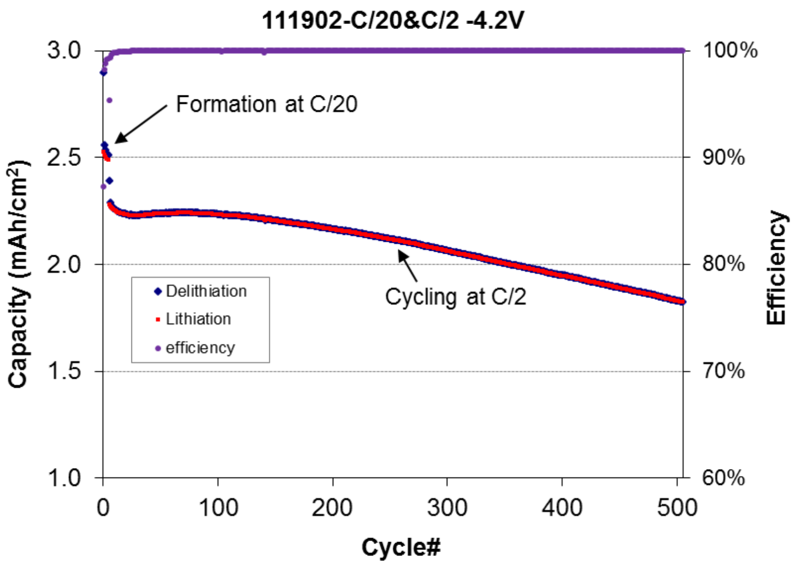
- Unique aspects of work:
  - Research focused on making high quality electrodes and cells
  - Ability to assess power capability of material in similar electrodes; determine sources of capacity (side reactions, phase changes, resistance rise) and power (ohmic, kinetic, and mass transfer resistance of cathode and anode) fade.

- Technical barriers addressed
  - Standard electrodes made and rate tested
  - Cycle life measured

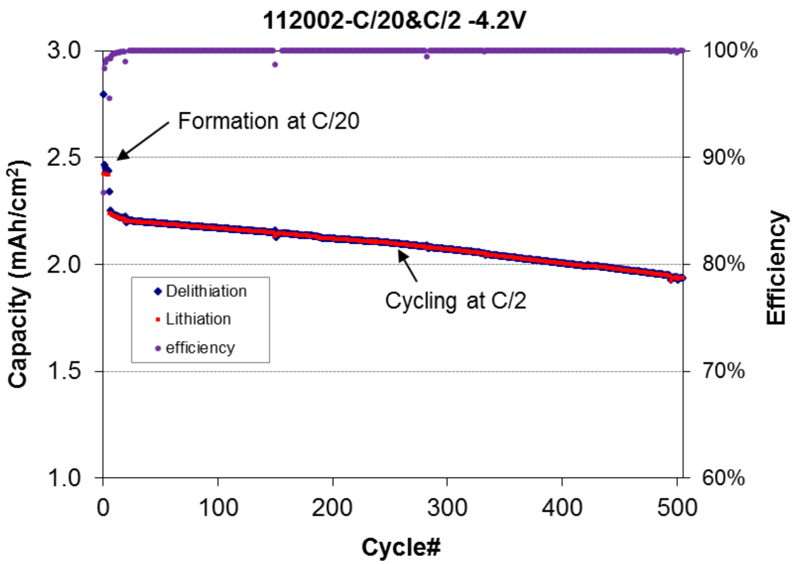
- Integration with ABR and BATT
  - Work closely with BATT PIs to identify promising materials
  - Work closely with ABR suppliers to identify next-generation materials

Technical Accomplishments: 1
Assessing BATT PI Materials

Scherson's nonflammable salt



Baseline Electrolyte



Baseline Electrolyte
+ VC + Flame retardant salt

No negative impacts on cycle life;
Encouraged to test in large cells for abuse characteristics.

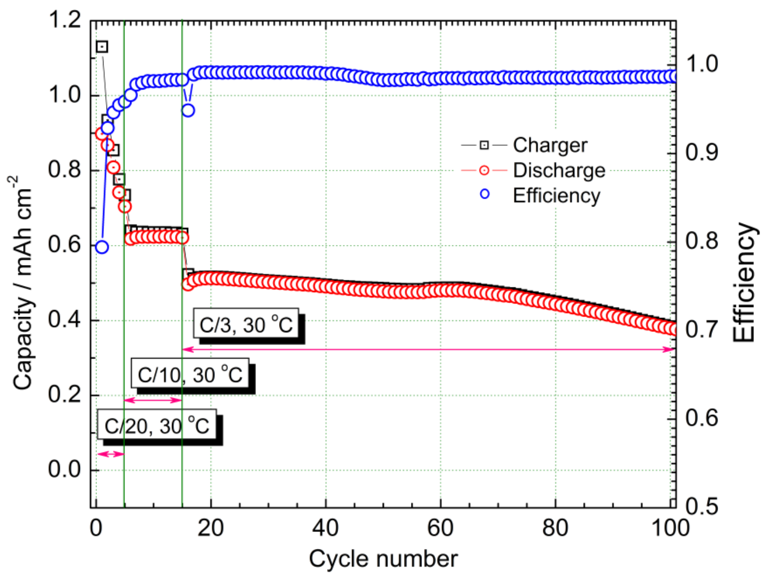
Technical Accomplishment: 2

Assessing BATT PI High-Voltage Materials

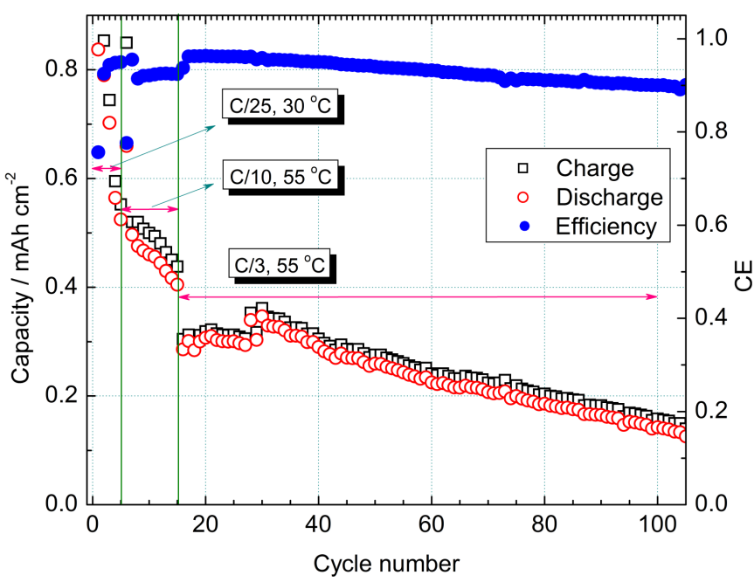
Baseline Material (NEI)

w/graphite anode

30°C



55°C

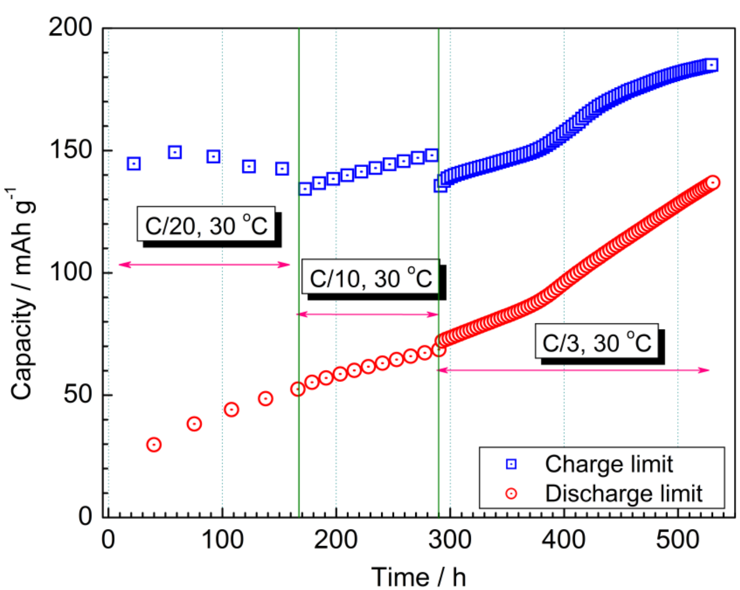


Half the capacity lost in both cells before C/3 testing; nearly all capacity lost in 100 cycles at 55°C

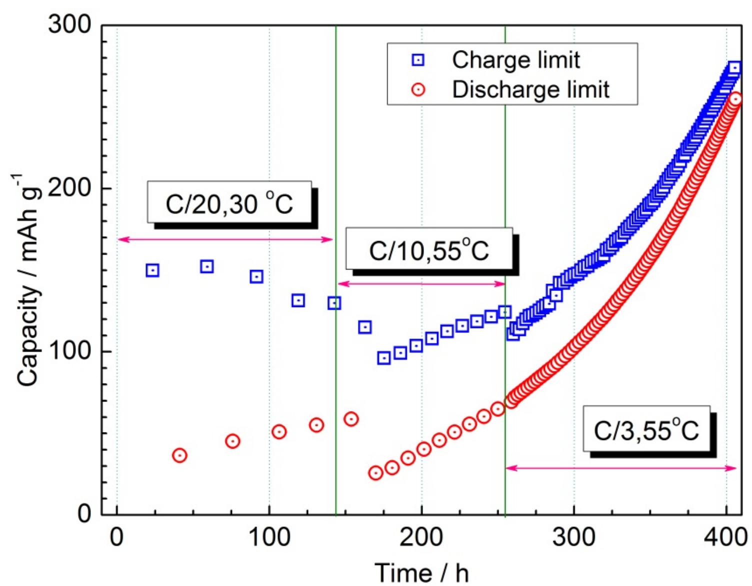
Technical Accomplishment: 2
Assessing BATT PI High-Voltage Materials

Baseline Material (NEI)
w/graphite anode

30°C



55°C



Side reaction on anode
constant at *ca*. 0.12 mA/g at 30°C

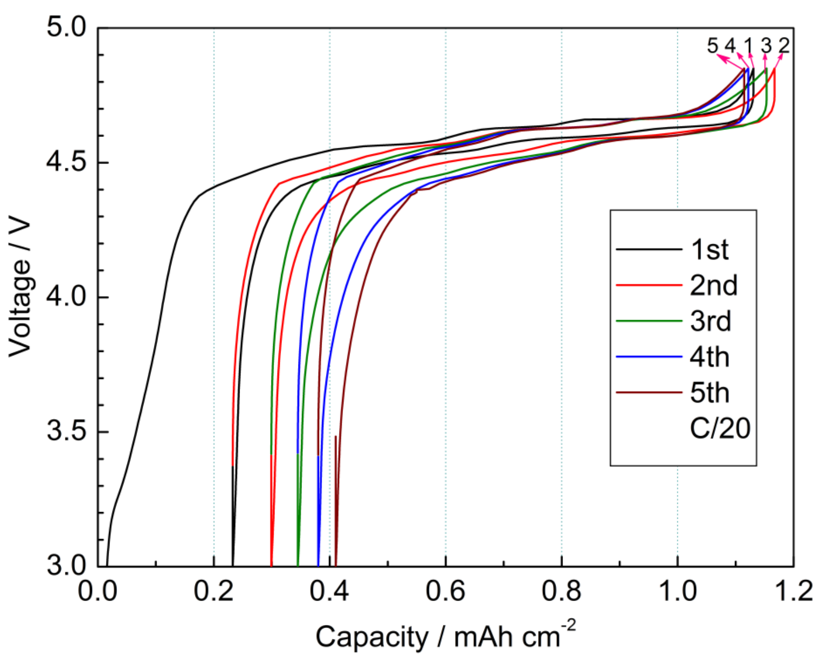
Same for cathode after first 5 cycles

Side reaction on anode
increases with temp.to *ca*. 0.51 mA/g at 55°C;

Charge limit diving rapidly, initially.
Side reaction on anode accelerates at C/3.

Technical Accomplishment: 2
Assessing BATT PI High-Voltage Materials

Baseline Material (NEI)
w/graphite anode



30°C

At 30°C the material experiences a phase transformation from a 2-phase material to a single phase material and the cell experiences a high first cycle inefficiency.
One sees the anode marching along while the cathode stays put.

Technical Accomplishment: 2

Assessing BATT PI High-Voltage Materials

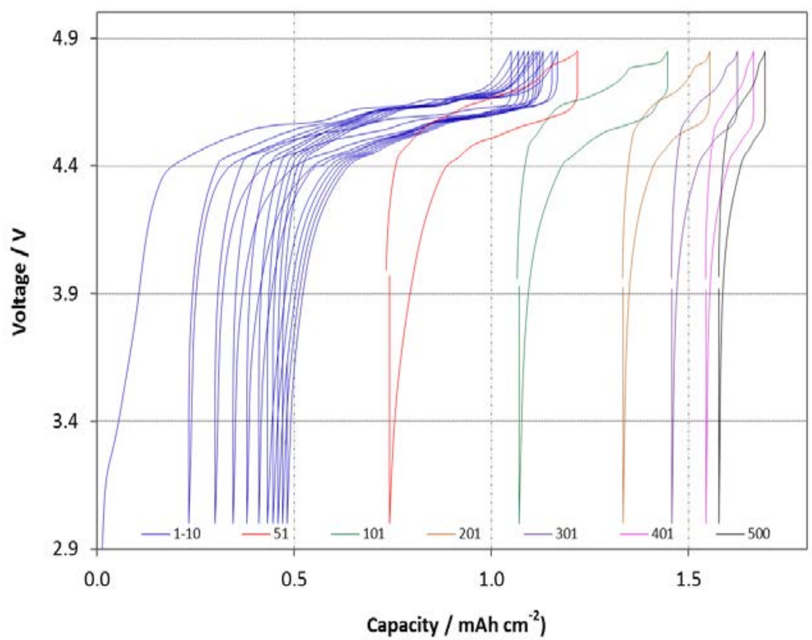
Baseline Material (NEI)

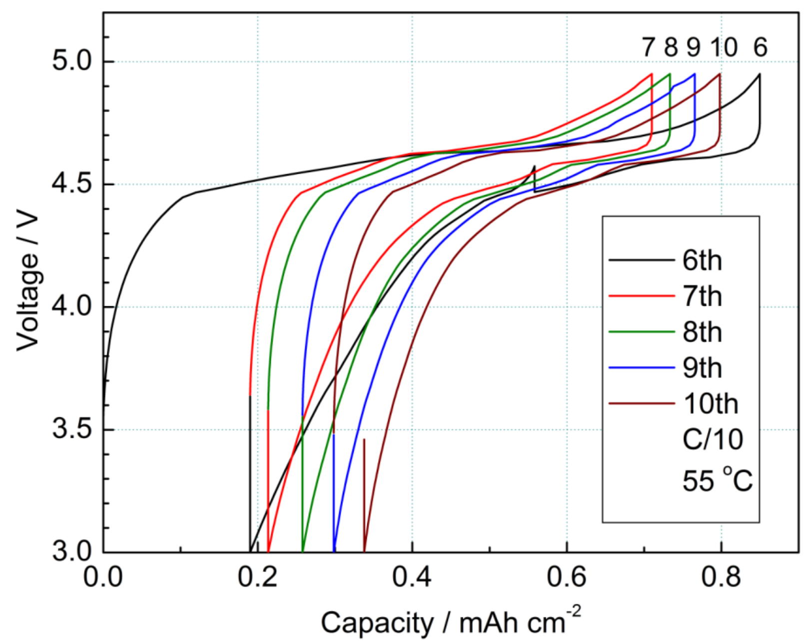
w/graphite anode

30°C

Cycles 6-10

55°C



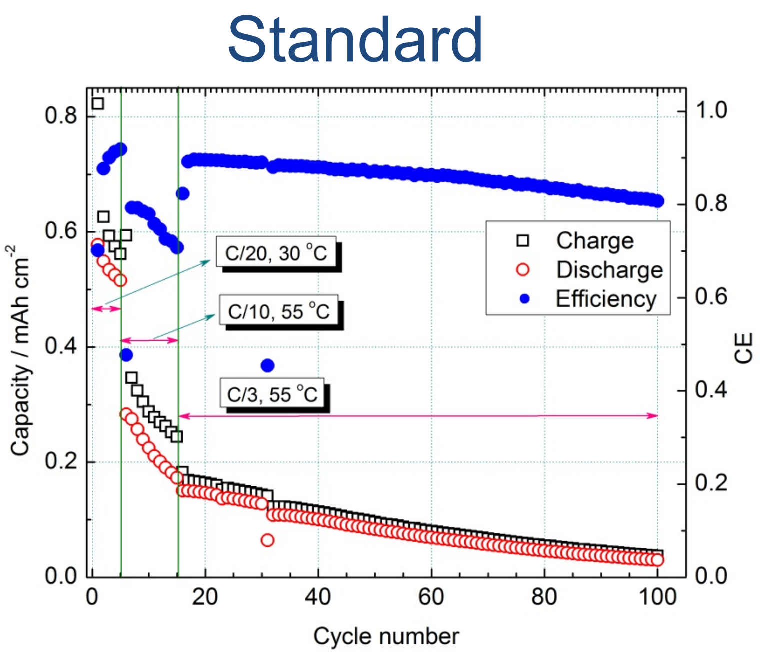


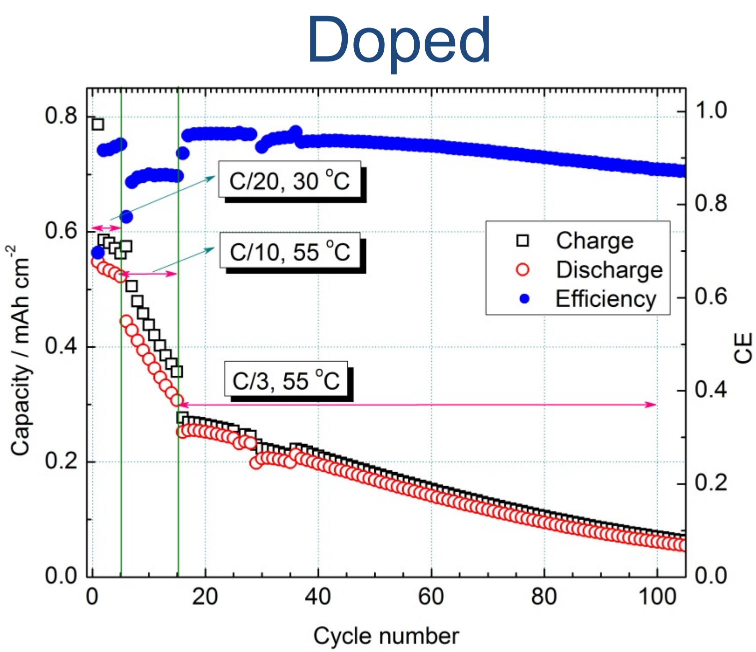
At 30°C the transformation appears complete as the rate is increased.
With the transition to 55°C the phase transformation is complete after 1 cycle and the cell experiences a second high first cycle inefficiency.

Technical Accomplishment: 2

Assessing BATT PI Two High-Voltage Materials

2 P.I. Materials @ 55°C



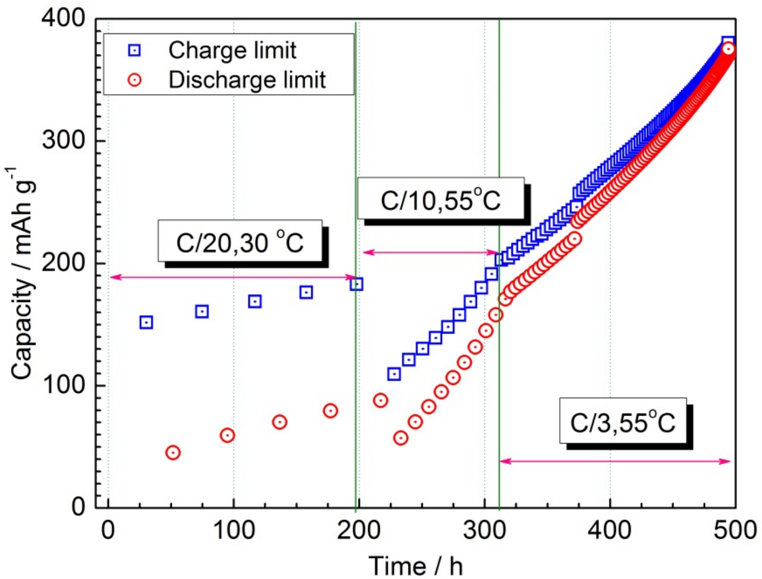


The doped material appears to hold up better through the first 15 cycles; both suffer the same fate upon subsequent cycling.

Technical Accomplishment: 2
Assessing BATT PI High-Voltage Materials

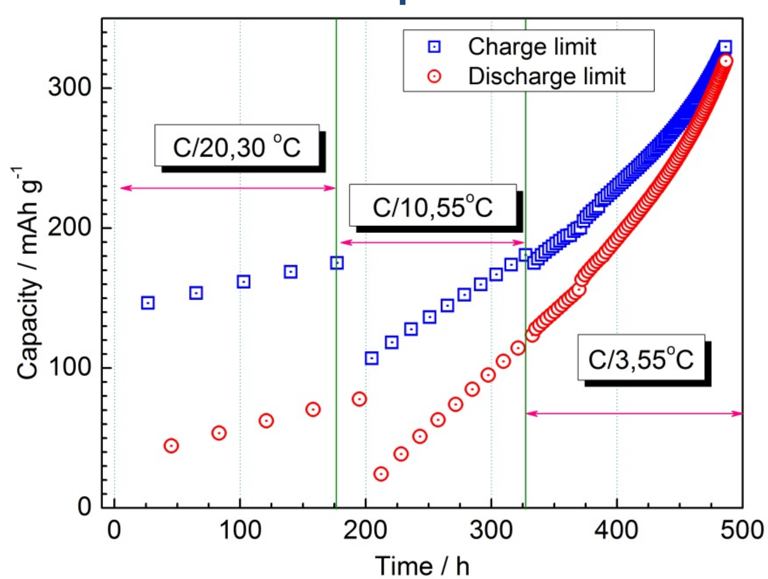
2 P.I. Materials @ 55^{o}C

Standard



Side reaction on anode *ca*. 1.25 mA/g before it accelerates at 375 hours.
Large capacity drop when rate increased from C/20 to C/10
Large irrev. loss when temperature rose from 30 to 55^{o}C.

Doped



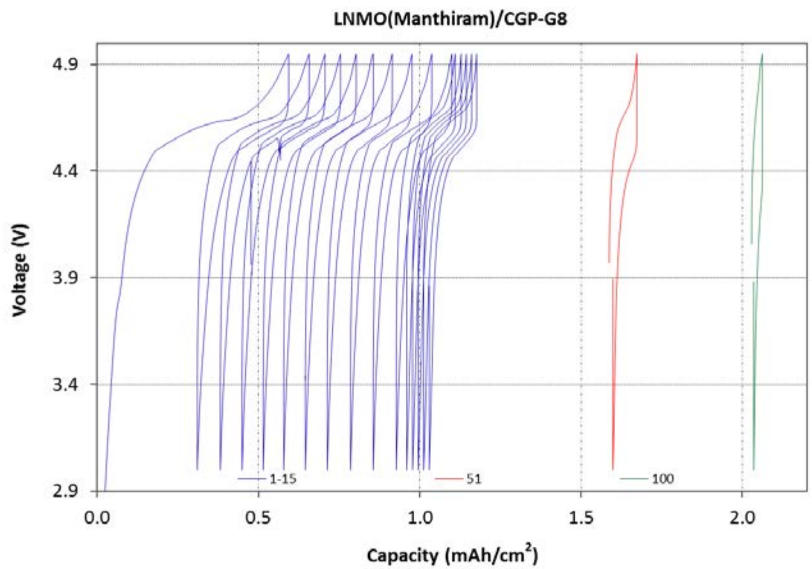
Side reaction on anode *ca*. 0.83 mA/g before it accelerates at 375 hours.

Not much loss with switch in cycling rates

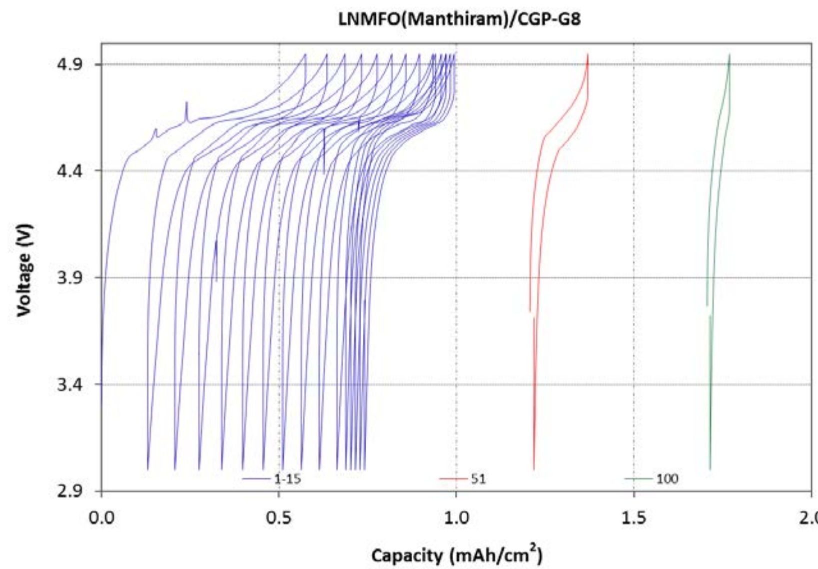
Technical Accomplishment: 2
Assessing BATT PI High-Voltage Materials

2 P.I. Materials @ 55^{o}C

Standard



Doped



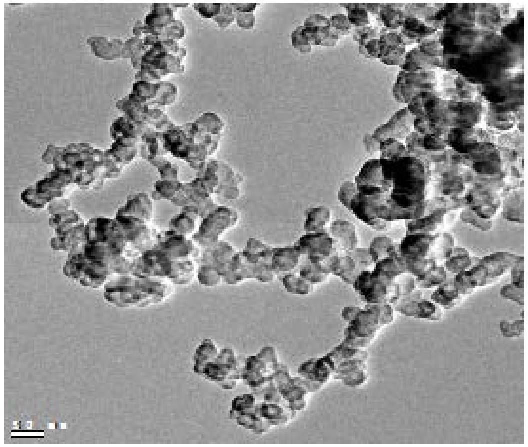
No phase change seen in the voltage curves during the first 10 cycles at 55^{o}C.

Technical Accomplishment: 3

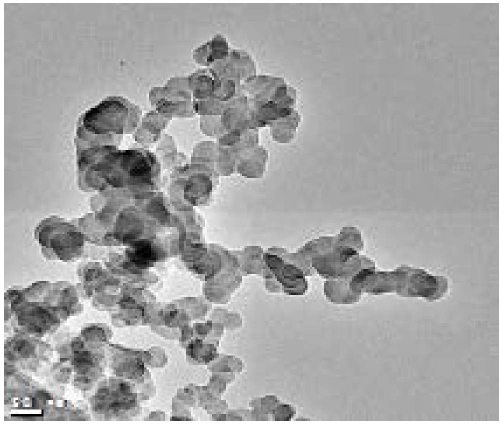
Assessing Supplier High-Voltage Materials

New Conductive Additives
from Timcal

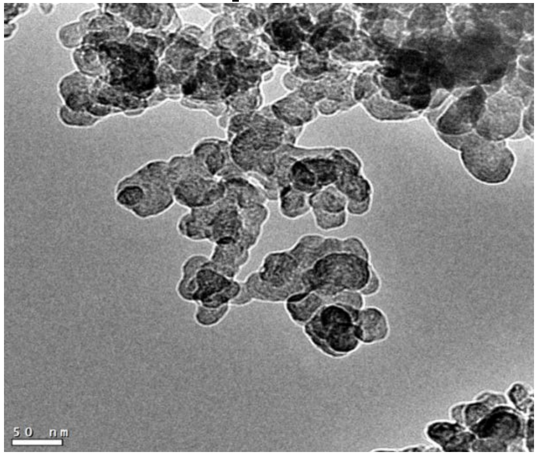
C65



C45



Super P

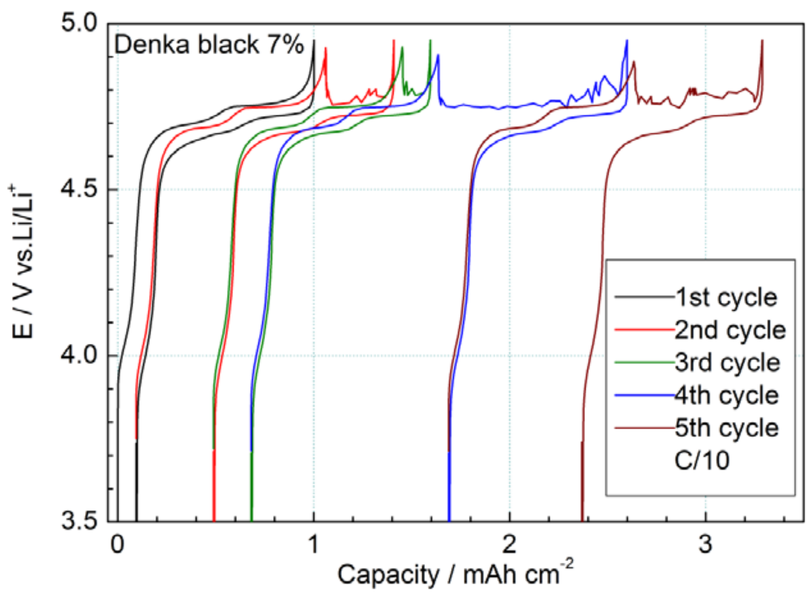


These high surface area carbons form chains which are integral to their performance

The Super P consists of the largest particles.

Technical Accomplishment: 3

Assessing Supplier High-Voltage Materials



- Carbon's to be tested
  - Acetylene black (AB, from Denka - baseline)
  - VGCF
  - Super P-Li (from Timcal)
  - Super C 65 (from Timcal)
  - Super C 45 (from Timcal)

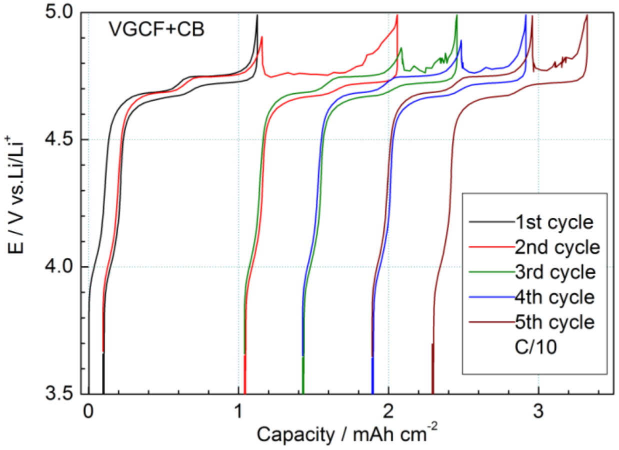
- Baseline cell conditions
  - LNMO/Li half-cell
  - Cathode: LNMO (NEI #3)/PVDF/ Conductive additive
  - $LiPF_6$/EC-DEC (Daikin, 1M, 1:2 vol)
  - Celgard 2400 separator Test rate: C/10
  - Cut-off potential: 4.99V

Large side reaction in the presence of Li counter electrode

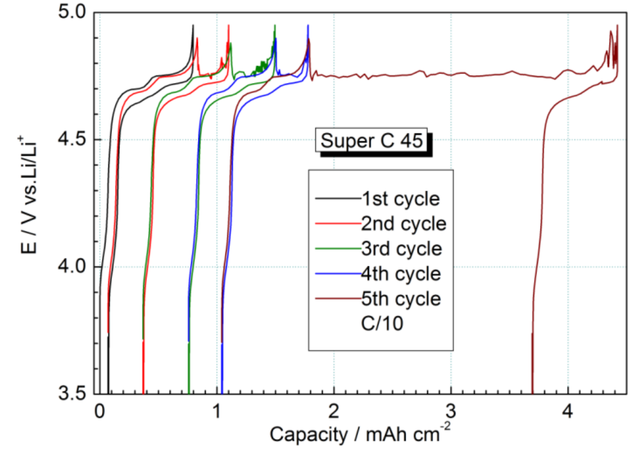
Technical Accomplishment: 3

Assessing Supplier High-Voltage Materials

VCGF+CB

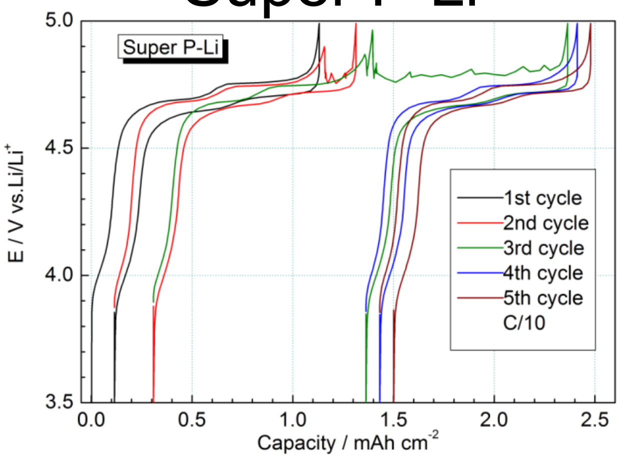


Super C45



~1 mAh/cm^2

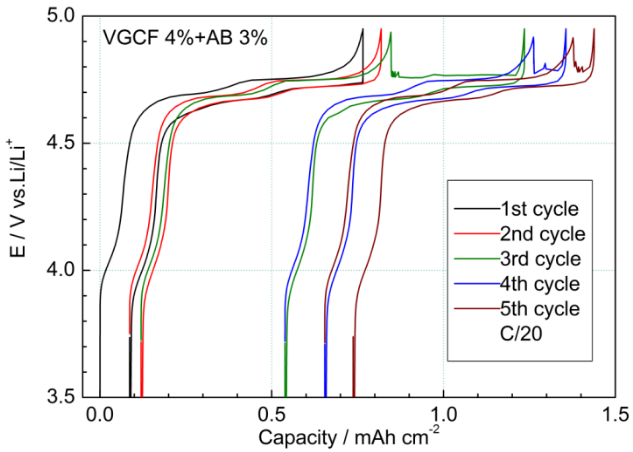
Super P Li



All of these carbons show erratic voltage behavior as a result of the production of a gas.

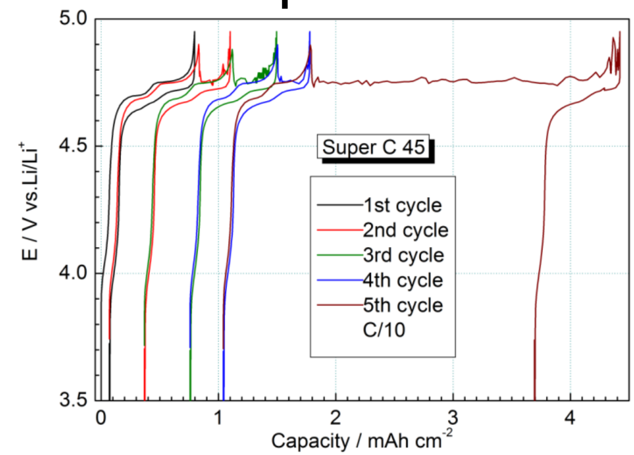
Technical Accomplishment: 3
Assessing Supplier High-Voltage Materials

VCGF+CB

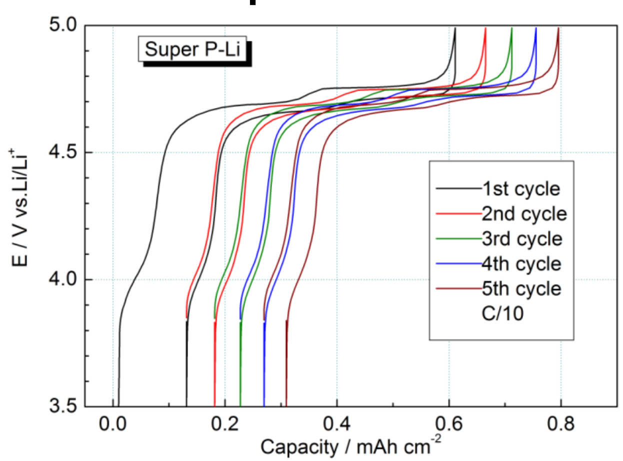


~0.6 mAh/cm²

Super C45



Super P Li



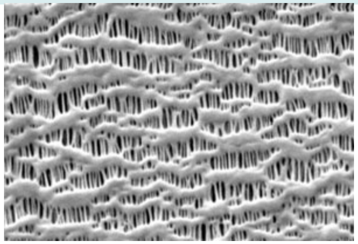
- Lower loading cathodes w/ Super P do not display the erratic voltage behavior.
- This is not seen for the low loading cathodes with C45.
- Lower loadings w/Super P form less CO_2 and can be reduced by the lithium.

Technical Accomplishment: 3

Assessing Supplier High-Voltage Materials

- Celgard 2400
- Celgard 2500
- Celgard 3501

Alternative Separators



Product	Thickness	JIS Gurley	Porosity	TD Shrinkage	Materials
2400	25 µm	620 seconds	Medium	0%	PP
2500	25 µm	200 seconds	High	0%	PP
3501	25 µm	200 seconds	High	0%	PP

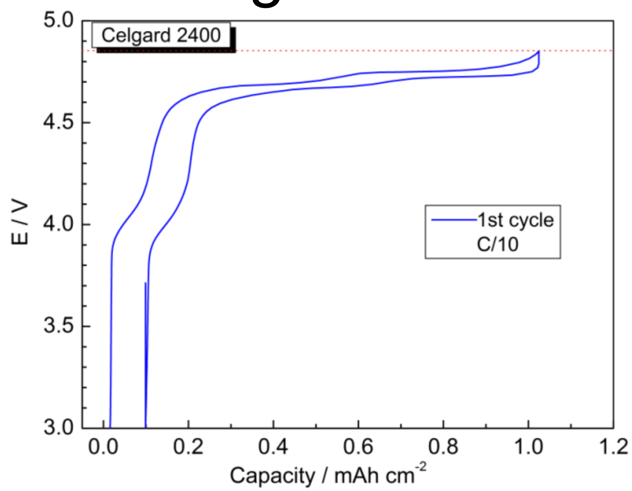
Cell Testing Materials and Protocol

- LNMO/Li half-cell
- LNMO (NEI #3)/PVDF/AB
- $LiPF_6$/EC-DEC (Daikin, 1M, 1:2 vol)
- Test rate: C/10
- Cut-off potential: 4.85V

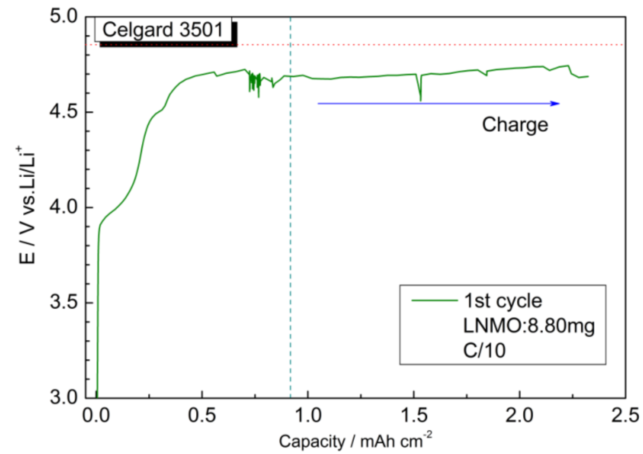
Technical Accomplishment: 3

Assessing Supplier High-Voltage Materials

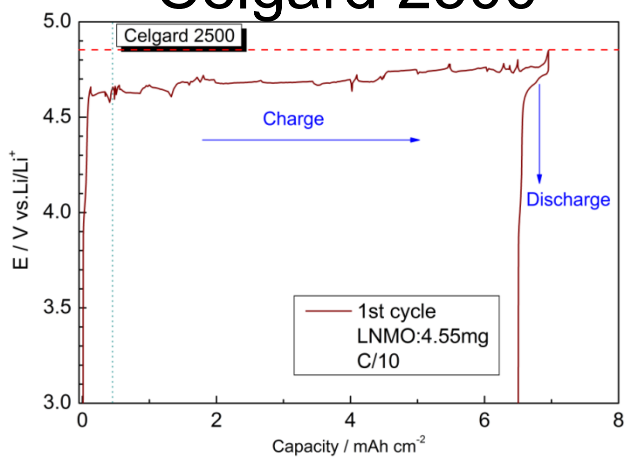
Celgard 2400



Celgard 3501



Celgard 2500



Separator with lower porosity and permeability resolves the erratic voltage issue during charge.

Collaboration and Coordination with Other Institutions

- NEI
  - Partner, Industry, outside VT, materials
- Daikin
  - Partner, Industry, outside VT, materials
- Umicore
  - Partner, Industry, outside VT, materials
- Conoco Phillips
  - Partner, Industry, outside VT, materials
- Timcal
  - Partner, Industry, outside VT, materials
- Celgard
  - Partner, Industry, outside VT, materials
- Case Western Reserve University
  - Partner, University, within VT, material exchange
- University of Texas
  - Partner, University, within VT, material exchange
- ANL
  - Partner, Federal Lab, within VT, information exchange
- SNL
  - Partner, Federal Lab, within VT, information exchange

Future Work

- Test additional BATT PI materials.
  - Focus on Electrolytes and Anodes the rest of this year
    - Electrolyte additive from ANL is under test.
    - A cathode material from LBNL is on its way
- Work with others to understand the acceleration of side reactions with cycling at 55^{o}C and screen possible alternative electrolytes.
- Verify the production and composition of a gas in the cell *via* the use of a mass spec. This may help identify the source of the gas.
- Test a cell where the gas is extracted during testing to see if the erratic cell behavior can be affected.
- Develop advanced electrolytes *via* the recently announced DOE FOA.

Summary

- Scherson's flame retardant salt additive shows no measureable negative impacts on cycleability.

- BATT PI's cathode materials show improvement in phase transition but still suffer at high temperature due to unstable electrolyte.

- The presence of high-surface area conductive carbon contributes to the amount of side reaction in the high voltage cathode.

- Cells with lithium show an erratic voltage during charge. We believe this is due to the formation of gas.

- Super P results in the least amount of erratic behavior.

- Cells of a low loading of 0.6 mAh/cm^2 and Super P cycle without the erratic effect of a gas.

- More porous separators result in more erratic cell behavior.

- Two theories:
    1. Products from the anode oxidize in the cathode to form gas (thicker electrodes = more surface area for CO_2 production from oxalate, separator limits oxalate crossover from anode).
    2. The gas is formed on the anode by some product produced in the cathode (thicker electrode results in more soluble product formed).

- Gas sampling may help sort this out.